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Determination of the sp^3 C content of a-C films through EELS analysis in the TEM

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Abstract

Electron energy loss spectroscopy (EELS) in a transmission electron microscope (TEM) was employed to estimate the sp^3 C content in magnetron sputtered H-free a-C coatings. The deconvolution procedure developed reduces considerably the error which is due to beam point spread function and sample thickness. The methodology has been applied to thin a-C films deposited through RF magnetron sputtering, and determined that, under the present values of ion current to the substrates ($<1 \text{ mA/cm}^2$), a variation in energy of the upcoming ions (achieved through a variation in applied substrate bias) has a negligible influence on the C atoms hybridization.

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Keywords: a-C; H-free; sp^3/sp^2 ; EELS; TEM

1. Introduction

Amorphous diamond-like-carbon (DLC) coatings consist of a mixture of sp^3 and sp^2 carbon structures, where sp^2 -bonded graphite-like clusters are embedded in an amorphous sp^3 -bonded carbon matrix [1]. They have been subject to studies since the 1970s and several different types of DLC have emerged. They can be roughly divided in hydrogenated (a-C:H) and hydrogen-free (a-C) DLCs. For a detailed study of the present status of the research in this field, reference is made to Refs. [2,3]. In the case where hydrogen atoms are present in the random network as bound to C, they stabilize the sp^3 hybridization, which is responsible for high hardness and rigidity of the network, but they decrease the connectivity between the sp^3 hybridized C sites, which has a strong influence on the film mechanical properties. Both hydrogenated and hydrogen-free DLCs can be metal doped (Me-DLC) or carbide doped (MeC-DLC). In the latter case, it has been shown that

nano-composite coatings can form; they combine low friction coefficient with high toughness and wear resistance, which renders them innovative and very attractive for wear resistant applications in the automotive industry. For a detailed study of these coatings, reference is made to Ref. [4,5]. The thermal resistance of these nano-composite coatings will clearly depend on the thermal stability of the a-C matrix. Avoiding the presence of H in the a-C network can lead to an improvement of the thermal stability of the material, and an increase in sp^3 C content has proved to bring about an additional improvement [6].

The mechanism of the formation of sp^3 -hybridized C is modeled as “subplantation”, where energetic C atoms are able to penetrate the material and subsequently bond in a highly-stressed tetrahedral (sp^3) configuration [3]. To penetrate the growing a-C network, the ions must overcome the C displacement energy, between 25 and 35 eV. This energy is considerably higher than the typical energy of evaporation deposition (0.3 eV) or sputtering (3–5 eV), but can be achieved via energetic deposition techniques such as PLD (atom energy up to 40 eV) or filtered cathodic vacuum arc (FCVA), in which a good portion of the upcoming C atoms is ionized, and a bias can be applied to the substrate to

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accelerate the C ions up to the desired energy. In the latter case, it has been determined that the final sp^3 fraction can be as high as 90% when the C ions energy is around 100 eV [3]. It has been reported [7] that high fractions of sp^3 C are also obtainable via magnetron sputtering/ion plating (MS/IP), but in this case the C penetration occurs via knock-on collisions with the energetic Ar ions.

Several methodologies have been developed for the estimate of the sp^3 fraction with the use of EELS that can be applied to hydrogen-free [8–10] and hydrogenated [11] pure a-C(:H) films, based on the analysis of the C K-edge structure.

This paper proposes a methodology for the systematic study of the variation of the sp^3 -hybridized C content which can diminish considerably the error due to peak broadening effects and thickness differences between different samples. Subsequently, the method is applied to study several a-C films obtained under different conditions of ion bombardment, to determine the influence of this parameter on the final coating properties for depositions performed with a balanced magnetron sputtering system.

2. Experimental

Thin a-C films were deposited using a planar RF balanced magnetron sputtering system (Edwards 306A) that provides typical ion current to the substrate in the range of 0.5–1 mA/cm². KBr pellets were fixed in the chamber at a distance of 60 mm from the surface of a graphite target (99.999% purity). The films' composition approaches 100 at.% C, oxygen is present as impurity in low concentration, around 2 at.%. The coatings were deposited without substrate rotation on the KBr pellets at two different locations: opposite to the center and to the border of the target, respectively. The chamber was first evacuated to 10^{-6} mbar pressure, and subsequently Ar gas was introduced to achieve a pressure of $5 \cdot 10^{-3}$ mbar for deposition. The substrates were sputter-cleaned for 5 min prior to deposition. Sputtering of the graphite target was then initiated with an applied power of 500 W. Coatings were grown up to a thickness of around 20 nm under different substrate bias values (between floating and 100 V). To determine the deposition time needed to reach the desired thickness for each value of substrate bias, thick coatings were

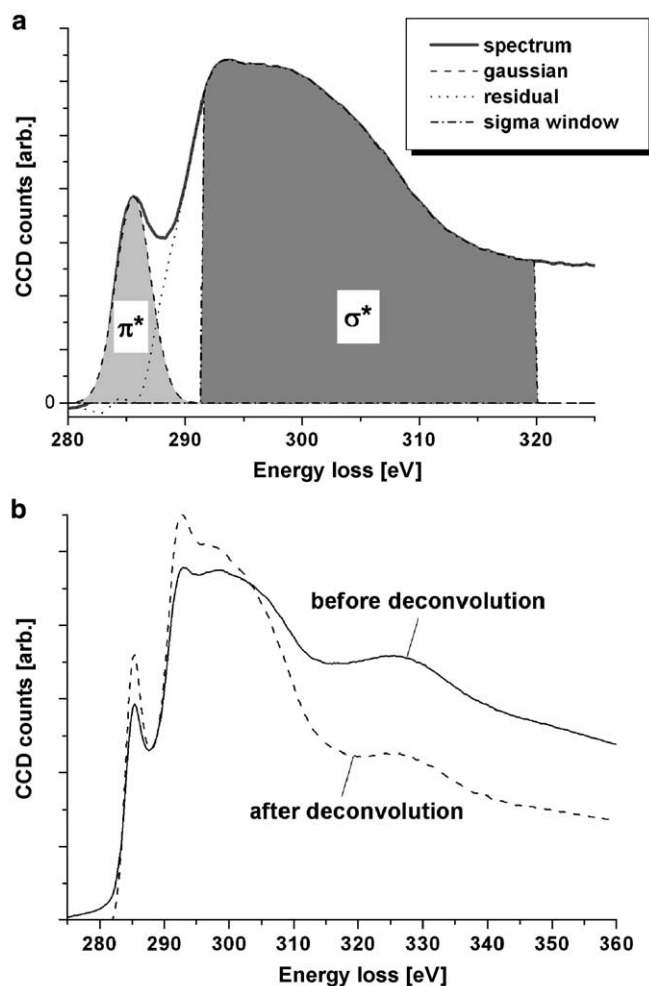


Fig. 1. (a) Decomposition of the C K-edge spectrum into π^* and σ^* features. The areas used for peak and edge integration are indicated. (b) C K-edge before and after deconvolution. The edge shape changes considerably after deconvolution.

deposited on Si substrates, whose thickness was determined through profilometry. It was concluded that the substrate bias influences the growth rate, and for the thin films deposition different deposition times were employed, ranging from 4 to 12 min, depending on the substrate bias applied, to obtain thin films of approximately constant thickness, around 20 nm. After deposition, each KBr pellet was immersed in de-ionized water, the thin coating flaked off, and was collected with a 3 mm diameter Cu grid (300 mesh). This procedure yielded electron-transparent films in the as-deposited state, as compared to the normal TEM sample preparation technique, i.e. ion milling with high-energy (2–4 keV) Ar ions, which would cause C phase transformations [12]. A JEOL-2010F-TEM (FEG, operated at 200 kV) was employed to measure the EELS spectra. EELS spectra were acquired for all samples in spectrometer image mode, over an area of about 300 nm², with a spectrometer channel resolution of 0.3 eV and with a narrow objective aperture to improve the signal to background ratio. The C K-edge was collected for 10 s. Subsequently, the zero loss peak and low loss portion of the spectrum was collected for 0.02 s. The beam convergence angle was not varied between the two acquisitions, avoiding modifications of the EELS scattering cross sections, and the overall integration time was kept low in order to avoid sample contamination effects from residual hydrocarbons present in the microscope chamber.

3. Results and discussion

In order to determine the sp³ fraction, the carbon K-edge portion of the spectrum is decomposed to compare the intensities of the σ^* and π^* features. The decomposition procedure is shown in Fig. 1a. The π^* feature is fitted with a Gaussian peak. The procedure provides suitable fits with very low residuals (dotted line in Fig. 1a). The σ^* feature is integrated within an energy window, that starts after the previously fitted Gaussian peak and terminates at a selectable value of the energy loss (320 eV in Fig. 1a). The fine-structure features of the EELS spectrum for the analyzed samples must be compared to the ones of a standard specimen that exhibits 100% sp² hybridization. The standard here chosen is a glassy carbon foil, which is known to exhibit 100% sp² hybridization, high purity and lack of long-range crystallinity. Spectra should be acquired for the standard specimen and the film of interest. By comparison of the values of the π^*/σ^* parameter, the sp² fraction in the coating (x) can be estimated using (from Refs. [9,10]):

$$\frac{(\pi^*/\sigma^*)_{\text{DLC}}}{(\pi^*/\sigma^*)_{\text{std}}} = \frac{3x}{4-x} \quad (1)$$

It is crucial to perform a proper correction of the spectra for multiple scattering and spectrometer point-spread function

before using Eq. (1), as this effect can alter the intensities of the π^* and σ^* features and hinder the comparison between spectra collected at different foil thickness. The spectra analysis consists in the subtraction of the spectrum background, after which a deconvolution procedure is performed. This procedure consists of two steps: a Fourier-ratio deconvolution procedure is performed first, which removes multiple scattering effects, estimated from the low loss portion of the spectrum. Consequently, the spectra are sharpened to correct for the point-spread function of the spectrometer, estimated from the shape of the zero loss peak. The appearance of a sample spectrum before and after deconvolution is shown in Fig. 1. After deconvolution, the intensity of the spectrum on the edge tail is reduced whereas the edge peaks are enhanced. The extent of the intensity variation is a function of the thickness of the area investigated in terms of t/λ , where t is the sample thickness and λ is the electron elastic mean free path, which depends on the characteristics of both the material and the electron beam. This dimensionless parameter can be easily determined from the analysis of the low-loss portion of the spectrum.

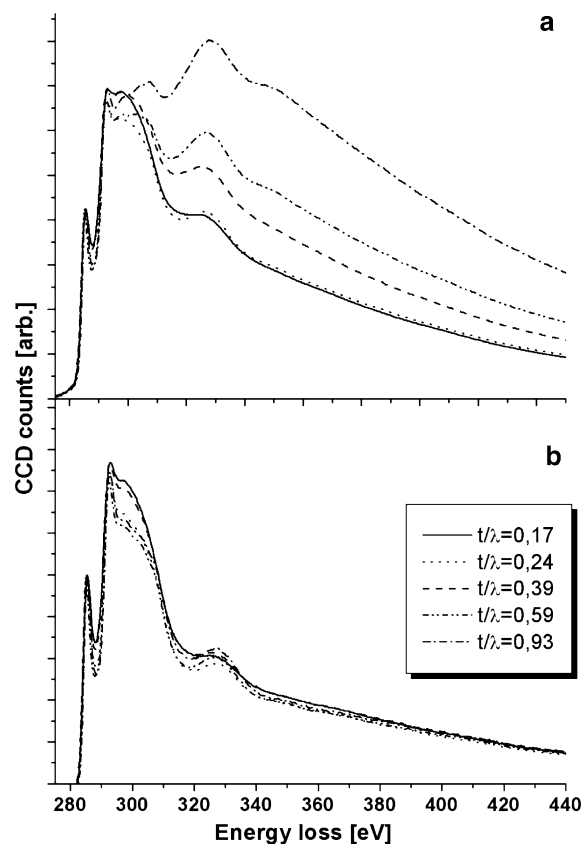


Fig. 2. Portions of the EELS spectrum for the glassy carbon standard recorded on areas of varying thickness (indicated): (a) the C K-edge spectra recorded at different sample thicknesses, their shape changes as a function of sample thickness; (b) after deconvolution the spectra assume the same shape.

Spectra of the C K-edge were recorded on different areas of the glassy carbon sample, which had different thickness, measured as t/λ , as indicated in Fig. 2. The carbon K-edge spectra after background subtraction differ in shape and intensity of the edge tail, which increases as the foils become thicker (see Fig. 2a). After deconvolution, the spectra shapes become more uniform (see Fig. 2b). The variation of the π^*/σ^* parameter after deconvolution, as a function of the σ^* integration window width, is reported in Fig. 3b. The error in the π^*/σ^* ratio for different window sizes is estimated from the standard deviation and reported in Fig. 3a as percentage of the average value for each σ^* window width. Values are reported as calculated after background subtraction, Fourier-ratio deconvolution and point-spread correction, these steps being applied one after the other. The deconvolution procedure reduces the error to 2–4%, with the narrower integration window width yielding the lowest error. The procedure described above was employed in the study of the H-free a-C films presented below.

The thickness of the various coatings was estimated by the t/λ parameter; the growth rate was then determined, in terms of the t/λ parameter, since the deposition time of all coatings was known. This procedure is very approx-

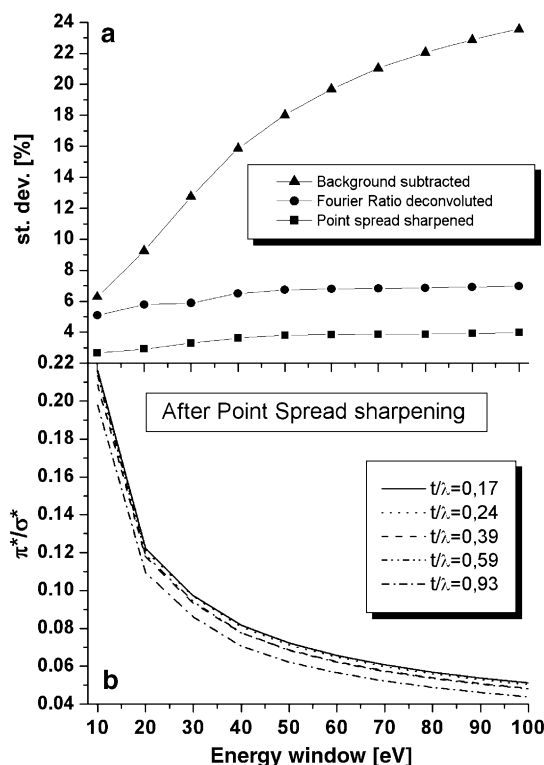


Fig. 3. (a) Standard deviation of the π^*/σ^* values among the different thickness investigated, given as percentage of the average value for each σ^* integration window. (b) Values of the π^*/σ^* parameter as a function of the width of the integration window, after deconvolution, for the spectra shown in Fig. 2. The values are roughly constant for each σ^* integration window width.

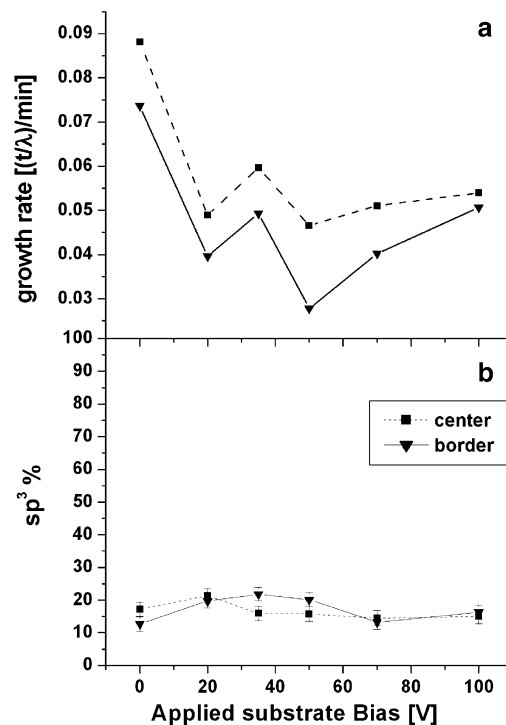


Fig. 4. (a) Variation of growth rate, in terms of t/λ , as a function of the different bias applied. Clearly applying external bias has the same influence on the film growth rate for both substrate locations, central and external, see text. (b) Variation of sp^3 C content as a function of the applied bias for both substrate locations. No clear sp^3 content variation is observed as a function of the applied substrate bias.

imate since the density of the a-C will vary as a function of the applied bias. Nevertheless, by plotting the so-determined growth rate vs. applied bias, as in Fig. 4, it is clear that the ion bombardment causes re-sputtering of the C from the growing film, since there is a clear decrease in growth rate when external bias is applied to the substrates. Furthermore, the growth rate of the films grown over the center of the target is always larger than that of the ones grown on the border, but their variation as a function of the applied bias is consistent. This clearly indicates that the difference in growth rate is due to a different intensity of C atoms flux in the 2 different locations, rather than to a difference in the intensity of ion bombardment. The sp^3 C content was determined for all coatings through the procedure explained above, using a 10 eV wide integration window. The variation of the sp^3 content as a function of the applied bias is minor, since it always remains in the range between 12% and 22%, without showing a clear trend as a function of the applied bias. This indicates that the formation of sp^3 C sites through knock-on collisions is not an effective process for the presently employed deposition conditions. These results are contradictory to what was observed by Schwan et al. in [7]. They observed sp^3 C contents higher than 80% with a 90 V substrate bias and an ion flux ratio (ratio of Ar ion flux to C neutral flux, Φ_i/Φ_n) value of

10. They observed that increasing the ion energy and the ion number over a certain threshold is accompanied by the generation of compressive stresses higher than 10 GPa and a sharp increase in the sp^3 C content. Since the presently employed deposition equipment is a balanced magnetron sputtering system, it can be inferred that the ion number will be lower in the present case than in the case of Schwan et al. This fact points to the importance of controlling the variation of the ion flux ratio during deposition more than the bias alone to manipulate the structure of the deposited films.

4. Conclusions

A procedure to collect and analyze EELS spectra has been developed, with the aim of reducing the error in the determination of the sp^3 C content in a-C films. The procedure was able to reduce the error in the determination of the π^*/σ^* parameter down to around 2%, and determined that the use of narrow integration windows for the σ^* edge is preferable since it yields lower errors. The procedure was applied to the study of sputtered a-C films deposited under different substrate bias conditions. The study determined that with the presently employed balanced magnetron sputtering equipment, no clear variation of sp^3 C occurs as a function of the applied substrate bias, but instead a sp^3 C content between 12% and 22% was measured in the range of bias investigated.

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